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FLOW CHANNEL CELL APPARATUS FOR HIGH RATE ELECTROLYSIS STUDIES

Dieter Landolt

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13 ABSTRACT

A simple flow channel cell apparatus is described which is suited for high rate electrolysis studies under well controlled hydrodynamic conditions. This design includes a discontinuously operated piston pump which presses the electrolyte through the electrochemical cell at linear velocities of up to 2000 cm/sec. An electrolyte volume of less than 2 liters is required for the operation of the apparatus. No metal parts except for the electrodes are in contact with the solution. Mass transfer characteristics of the flow channel cell have been determined by measuring limiting currents for the reduction of ferricyanid.

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flow channel apparatus						
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ABSTRACT

A simple flow channel cell apparatus is described which is suited for high rate electrolysis studies under well controlled hydrodynamic conditions. This design includes a discontinuously operated piston pump which presses the electrolyte through the electrochemical cell at linear velocities of up to 2000 cm/sec. An electrolyte volume of less than 2 liters is required for the operation of the apparatus. No metal parts except for the electrodes are in contact with the solution. Mass transfer characteristics of the flow channel cell have been determined by measuring limiting currents for the reduction of ferricyanid.

Introduction

The experimental investigation of electrochemical processes proceeding at very high rates (current densities of several amperes per square centimeter) requires an experimental setup which provides for well-controlled high mass transfer rates at the working electrode and for a low ohmic resistance between working electrode and counter or reference electrodes. Electrochemical flow channel cells are particularly suited to fulfill these requirements[1] provided they contain a sufficiently long hydrodynamic entrance length upstream from the electrodes for establishing fully developed velocity profiles. Unfortunately, the presence of a hydrodynamic entrance length leads to substantial pressure losses when high linear velocities are employed. For this reason, previously designed flow channel cells required large pumps, and many gallons of electrolytes had to be recirculated through an elaborate piping system. For electrochemical studies it would be desirable to have a clean and simple system, requiring only small quantities of solution with no metallic parts in contact with the electrolyte except for the electrodes. Up to now this has been possible only at the loss of well-defined hydrodynamics[2]. A new device is described here which fulfills all of the different requirements described. It consists of a piston pump and a rectangular flow channel cell in which linear electrolyte velocities of up to 2000 cm/sec are reached with fully developed velocity

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(1) D. Landolt, R. H. Muller, Ch. W. Tobias, J. Electrochem Soc., 16, 1384 (1969).

(2) D. Landolt, R. H. Muller, Ch. W. Tobias, J. Electrochem. Soc., 118, 40 (1971).

profiles at the electrodes. The compact design which requires less than 2 liters of electrolyte to be used includes no metal parts besides the electrodes in contact with the solution. The apparatus has been used successfully for steady state as well as for fast transient high rate metal dissolution studies. Quantitative data characterizing mass transfer conditions prevailing at the working electrode have been determined by limiting current measurements for the reduction of ferricyanid and are presented here.

General Description of the Device

The apparatus (Figure 1) consists of a heavy steel frame on which are mounted a variable speed motor drive unit, a PVC pump cylinder and the electrochemical cell. A separate 2 liter glass flask serves as electrolyte storage reservoir. Operation of the device is discontinuous. The electrolyte is drawn from the reservoir into the pump cylinder which has a capacity of 1.2 liters. The cell bypass valve is opened for that purpose. The valve is then closed and the direction of the motor is reversed. The advancing piston presses the electrolyte through the electrochemical cell, back into the reservoir. Discharge time can be varied from approximately 50 minutes to 38 seconds.

Drive Unit

The motor drive unit[3] consists of a shunt wound 1/3 hp DC motor, a speed control unit and a gear reductor. The rated output torque is

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(3) Radiotrol Systems VE33, Boston Gear Division of North American Rockwell, Quincy, Mass.

is 1075 inch/lb at 0.3 to 8.8 RPM. The output of the drive unit is translated into a linear motion of the pump piston by a rack and pinion assembly involving three spur gears of 2 inch, 8 inch and 1.25 inch pitch diameter. Two modifications are incorporated into the commercial drive unit. (i) In order to provide for better reproducibility of dial settings, the original speed indication dial knob is replaced with one with finer divisions. (ii) Limit switches are incorporated into the control circuit as shown schematically in Figure 2. Whenever the piston stroke reaches its maximum limit, the limit switches are activated by a pin protruding from the rack. Thus the motor is shut off automatically at the end of each filling or displacement operation of the pump. The pumping unit consists of a cylinder of 10.2 cm inner diameter, 14 cm outer diameter and 25 cm overall height, mounted vertically on the steel frame. The cylinder is machined from a solid block of PVC. Pumping action results from the movement of a teflon piston (5.1 cm high and 10.2 cm in diameter) which is fixed to the drive rack by means of stainless steel plates. Two neoprene o-rings with teflon slipper seals prevent electrolyte leakage. Stroke length is 15.2 cm. A 0.32 cm hole capped with a nylon fitting is drilled through the piston to facilitate drainage of the apparatus. Commercial nylon tube fittings[4], and 0.32 cm diameter nylon tubing is used for circulating the electrolyte between pump cell and reservoir. Two nylon valves[5] rated for 250 psi are used for closing off the flow through the cell or bypass when desired.

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(4) "Swagelock" 1/8" diam., Crawford Fittings Ltd., Niagara Falls, Ontario, Canada.

(5) Nupro V Series, Nupro Company 15635 Saranac Road, Cleveland, Ohio

Electrochemical Cell

The electrochemical cell (Fig. 3) consists of two rectangular PVC blocks of 15.6 x 5.2 x 1.8 cm separated by a 0.534 cm. thick teflon spacer and backed by two stainless steel plates. The lower plate protrudes from both ends of the cell and is used for mounting the cell on the apparatus steel frame. The cell assembly is held together with eight brass screws. Three steel pins serve for exact positioning of the cell parts with respect to each other. The teflon spacer is cut out in the center in order to provide a flow path for the electrolyte past the electrodes. O-rings are used for preventing any leakage between teflon spacer and PVC blocks. Nylon fittings[4] fixed to the cell bottom provide solution inlet and outlet. The leading edge of the working electrode is positioned 7 cm down stream from the flow channel inlet. With the channel dimensions of 0.317 x 0.0531 cm, this distance corresponds to 77 hydraulic diameters (defined by 4 x cross section/circumference). This length is enough to guarantee fully developed velocity profiles at the electrodes under both laminar and turbulent flow conditions[6][7].

The rectangular electrodes of 1.02 x 0.317 cm area are epoxy cast into cylindrical PVC holders of 1.9 and 1.58 cm diameter, respectively. The electrode holders contain a notch for aligning the electrodes parallel to flow direction. An o-ring seal arrangement and a set screw (not shown in Fig. 3) serve for sealing the electrodes and holding them in place.

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(6) F. S. Bromfield,"The Hydrodynamic Entry Length in Rectangular Channels,"Ph.D. Thesis, Univ. of Washington, 1964, p 30.

(7) R. B. Bird, W. E. Stewart and E. N. Lightfoot, Transport Phenomena, John Wiley, 1960, p 47.

The procedure of inserting and aligning the electrodes is simple and leads to accurate positioning with respect to the channel wall. After grinding or polishing, the larger diameter holder is inserted first by pressing it against the teflon spacer and tightening the o-ring seal and the set screw. Then the smaller diameter electrode holder is inserted the same way. The described design allows for easy regrinding and reuse of the electrodes, and also different electrode sizes such as electrodes of shorter length can be employed with the same holder dimensions. In order to allow for electrode potential measurements, a small capillary hole is drilled upstream from the working electrode providing for an electrolyte connection to the reference electrode compartment. Commercially available half-inch diameter calomel electrodes can be mounted in this compartment by means of an o-ring seal arrangement. A dynamic hydrogen reference electrode[8] consisting of two platinized platinum wires cast into a 1.27 cm diameter PVC holder has also been used. The use of the latter reference electrode together with its short distance from the working electrode provides for a low impedance circuit, well suited for fast transient studies.

Operating Characteristics

At the high linear velocities employed, considerable pressure builds up in the apparatus. This is evidenced by the data of Figure 4 obtained by connecting a pressure gauge to the pump cylinder outlet. The increase in pressure is found to be approximately proportional to the square of the

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(8) J. Giner, J. Electrochem. Soc., 111, 376 (1964).

flow rate as predicted by simple hydrodynamic considerations. The data indicate that the pressure remains well below the rated operating limit of the tubing system which is 17 atm. In order to prevent possible damage to the apparatus which, for example, might arise from accidentally closing both outlet valves, a simple safety device was installed in the pump cylinder drainage outlet. It consisted of a nylon diaphragm inserted into a standard fitting. At pressures above approximately 17 atm the diaphragm bursts, thus relieving the pressure.

The mass transfer characteristics of the apparatus were determined by limiting current measurements of the reduction of ferricyanid. For that purpose a solution containing 0.05 mole/liter potassium ferricyanid, 0.1 mole/liter potassium ferrocyanid and 2 mole per liter sodium hydroxide was prepared from reagent grade chemicals using double distilled water. The solution which was never kept for more than 12 to 15 hours was deaerated by bubbling nitrogen through it. It was stored under exclusion of light by wrapping the electrolyte reservoir bottle of the apparatus with aluminum foil. Experiments were carried out at 25.5 ± 0.5°. 1.02 x 0.317 cm nickel electrodes were used. Pretreatment of the cathode consisted of grinding with 400 carborundum, washing with detergent and water and subsequent cathodic preelectrolysis in 1 M NaOH at 20 mA/cm^2 for approximately 3 minutes. Because of observed poisoning of the nickel cathode, the pretreatment had to be repeated frequently. A commercial unit consisting of potentiostat, function generator and xy recorder was used for the experiments[9]. Examples of current potential curves measured at a scan rate of 100 mV/sec are given in Figure 5. A broad limiting

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(9) PAR 17C Electrochemistry Unit, Princeton Applied Research Corp., Princeton, N. J.

current plateau exists which is most pronounced at low flow rates. A few limiting current determinations were also made by applying a constant potential of -900 mV vs. SCE and recording the resulting current as a function of time at different flow rates. Care was taken in all experiments to eliminate any effects of electrode poisoning.

The usefulness of mass transfer data is enhanced by presenting them in dimensionless form. Such is done is Figure 6. The dimensionless quantities, Nusselt number, Reynolds number and Schmidt number are defined by

$$Nu = \frac{i_\ell D_h}{FC_o D} \quad , \qquad Re = \frac{uD_h\rho}{\eta} \quad , \qquad Sc = \frac{\eta}{\rho D}$$

Here i_ℓ is the measured limiting current density, D_h the hydraulic diameter, F the Faraday constant, C_o the ferricyanide concentration, D the diffusion coefficent of ferricyanid, u the linear velocity, ρ the density, η the viscosity. In order to calculate the above dimensionless numbers for the present experiments, the following numerical values were used[10]

$$D = 5.06 \times 10^{-6} \text{ cm}^2/\text{sec}, \quad \eta = 1.467 \times 10^{-2} \frac{\text{g}}{\text{cm sec}} ,$$

$$\rho = 1.107 \frac{\text{g}}{\text{cm}^3}$$

No experimental mass transfer data for channel dimensions as small as those of the present apparatus have been published hitherto in the literature.

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(10) E. Adam, "Zur Kenntnis des Stofftransportes an gasgespulten Electroden und deren Optimierung," Ph.D. Thesis Nr 4047 ETH, Zurich, Switzerland 1967.

However, dimensionless mass transfer correlations for laminar and turbulent flow conditions in larger pipes and channels are well known. For laminar flow, mass transfer rates are given by[11]

$$Nu = 1.85 \left(ReSc \frac{D_h}{L}\right)^{1/3}$$

For turbulent flow in pipes with fully developed velocity and mass transfer profiles a relation

$$Nu = 0.0789 \sqrt{f}\, ReSc^{1/4}$$

has been found useful[12][13]. The friction coefficient f can be estimated from $f = (0.079/Re^{1/4})$. The two theoretical relations are shown by the drawn lines in Figure 6. Except for the transition region $2000 < Re < 3000$, the experimental points coincide very well with the dimensionless correlations given.

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(11) J. Newman, Ind. Eng. Chem., 60, 12 (1968).

(12) R. B. Bird, W. E. Stewart and E. N. Lightfoot, Transport Phenomena, John Wiley, 1960, pp 402-3

(13) P. Van Shaw, L. P. Reiss, and T. J. Hanratty, AIChE Journal, 60, 12 (1968).

Acknowledgment

The author is greatly indebted to Bill Griffith of the UCLA Engineering R & D shops who did the mechanical work of building the apparatus. Without his careful work and his contribution of many useful design ideas, the device could not have been realized in its present form. Financial support was provided by the Office of Naval Research under Contract No. NOOO 14-69-A-0200-4029.

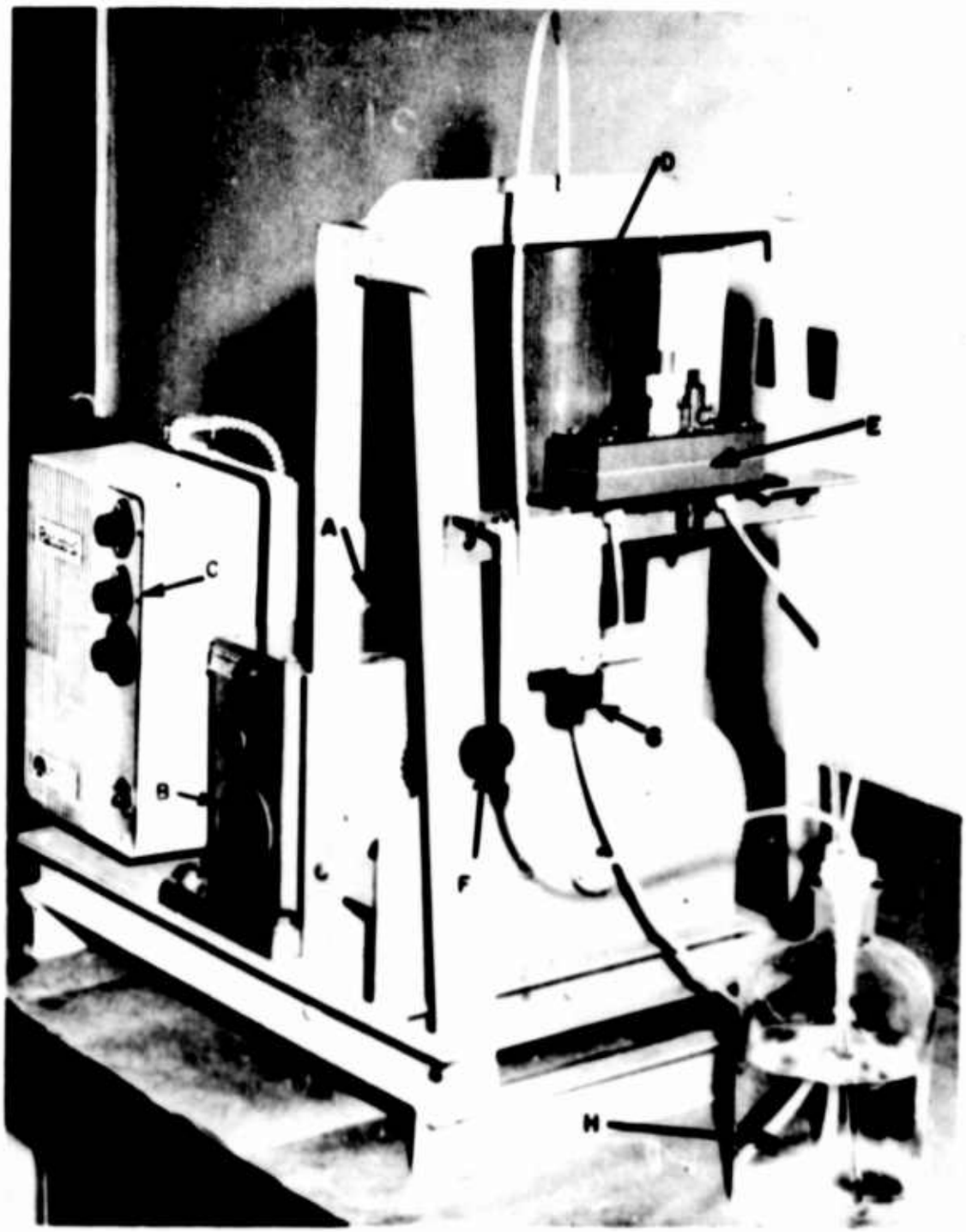
List of Figures

Q electrolyte outlet

Fig. 4 Pressure buildup in apparatus as a function of linear flow velocity in cell

Fig. 5 Current potential curves for cathodic reduction of ferricyanid at different flow rate. Potential scan rate = 100 mV/sec

Fig. 6 Mass transfer characteristics of flow channel cell derived from measured limiting currents for ferricyanid reduction. Solid lines represent mass transfer rates predicted for laminar and turbulent flow by the correlations given in the text.



A.	Motor	E.	Electrochemical Cell
B.	Gear reductor	F.	Bypass valve
C.	Control unit	G.	Cell valve
D.	Pump cylinder	H.	Electrolyte reservoir

Figure 1. General View of Flow Cell Apparatus

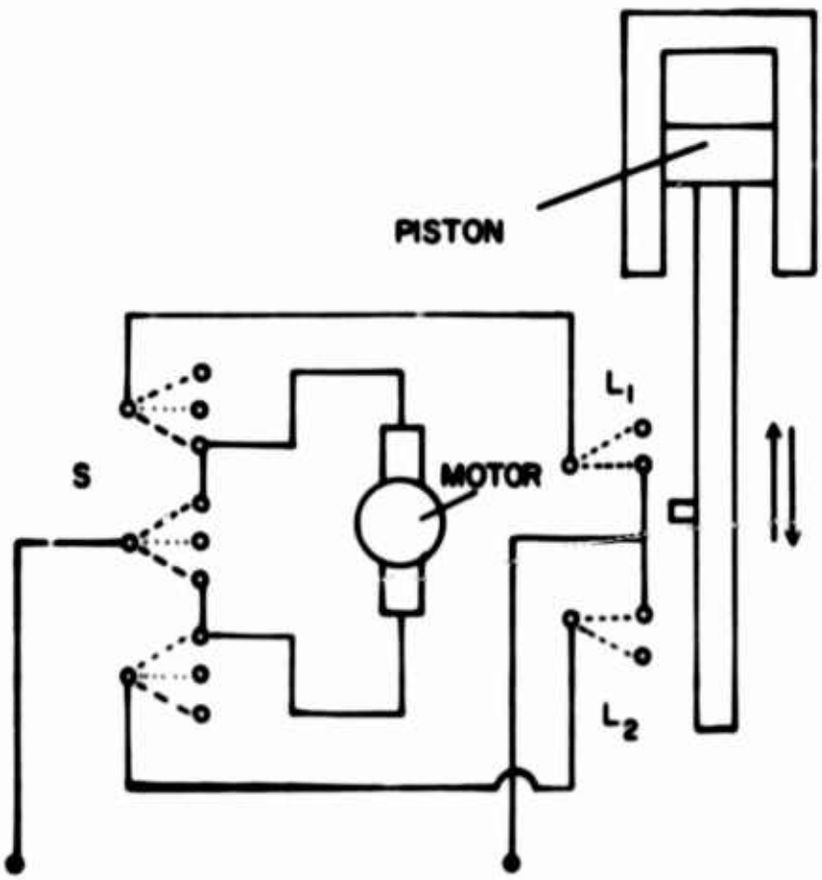
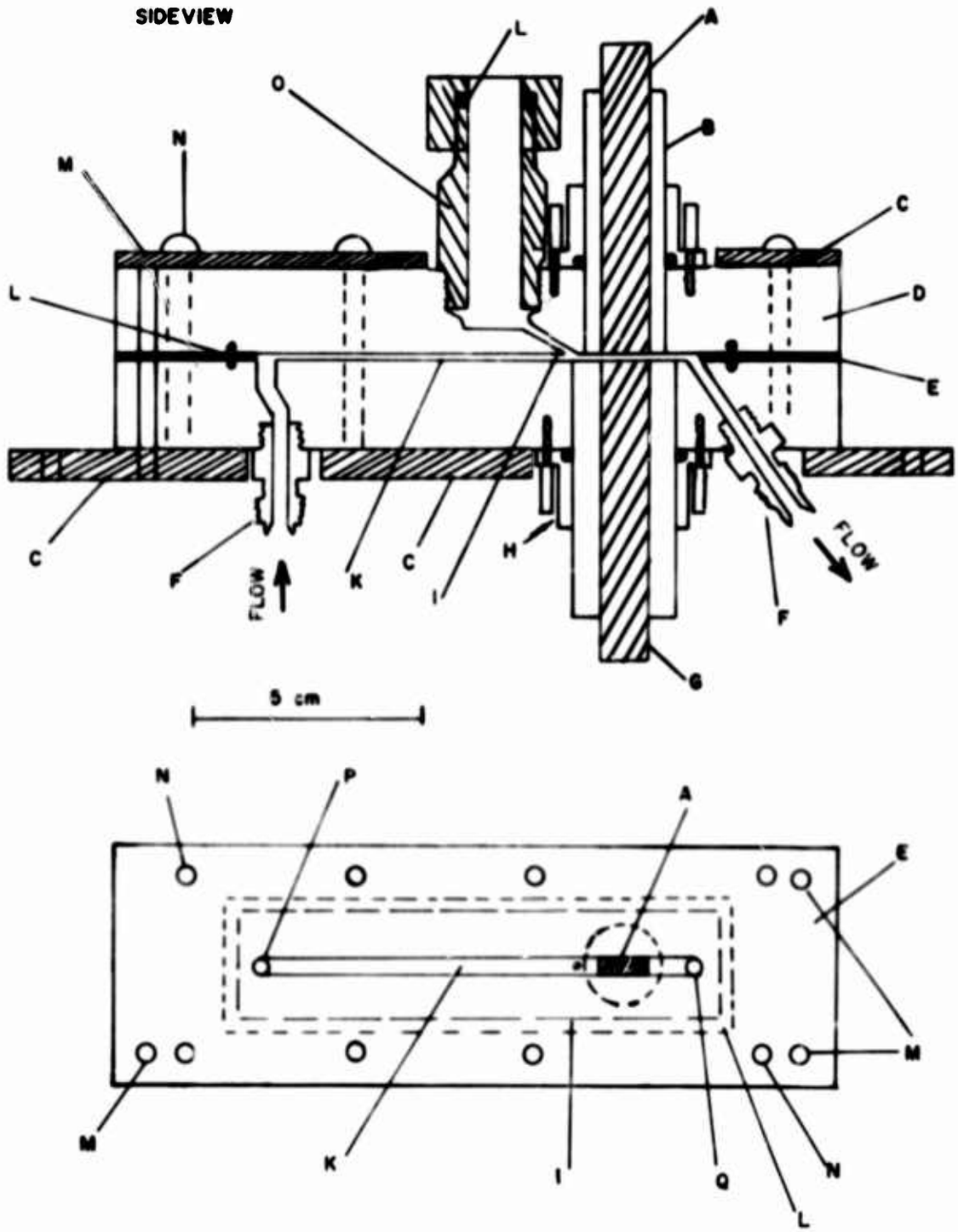


Figure 2. Schematic of Switching Arrangement with Control Switch S (forward, stop, reverse) and Limit Switches L_1 and L_2



A. Working electrode cast in PVC insert B
C. Stainless steel backing plate
D. PVC block
E. Teflon spacer
F. Nylon fitting
G. Counter electrode
H. Sealing arrangement with o-rings
I. Capillary to reference electrode compartment
K. Electrolyte flow channel
L. O-ring seal
M. positioning pin
N. Brass screws
O. Nylon insert (reference electrode holder)
P. Electrolyte inlet
Q. Electrolyte outlet

Figure 3. Electrochemical Flow Channel Cell (Schematic)

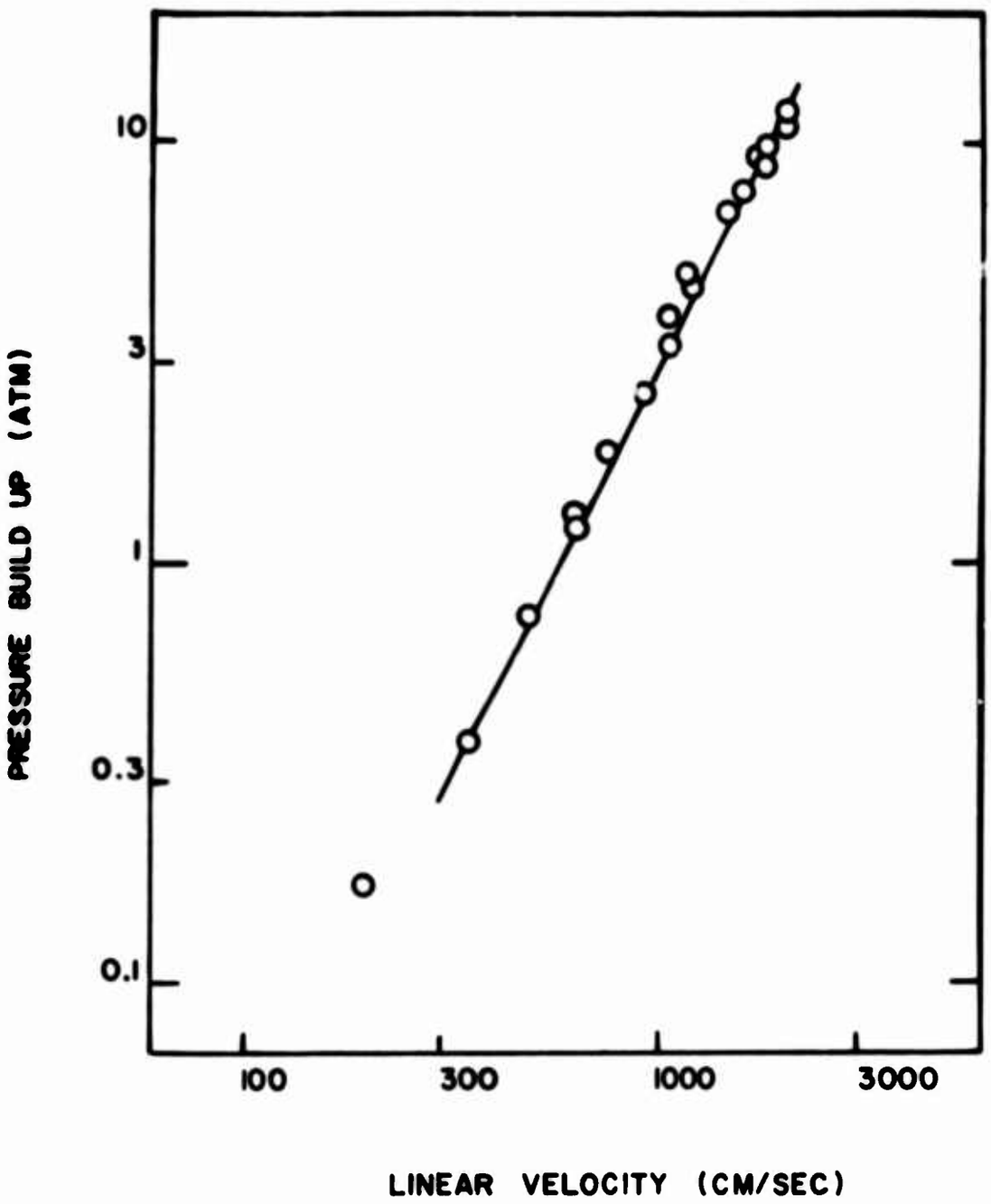


Figure 4. Pressure Buildup in Apparatus as a Function of Linear Flow Velocity in Cell

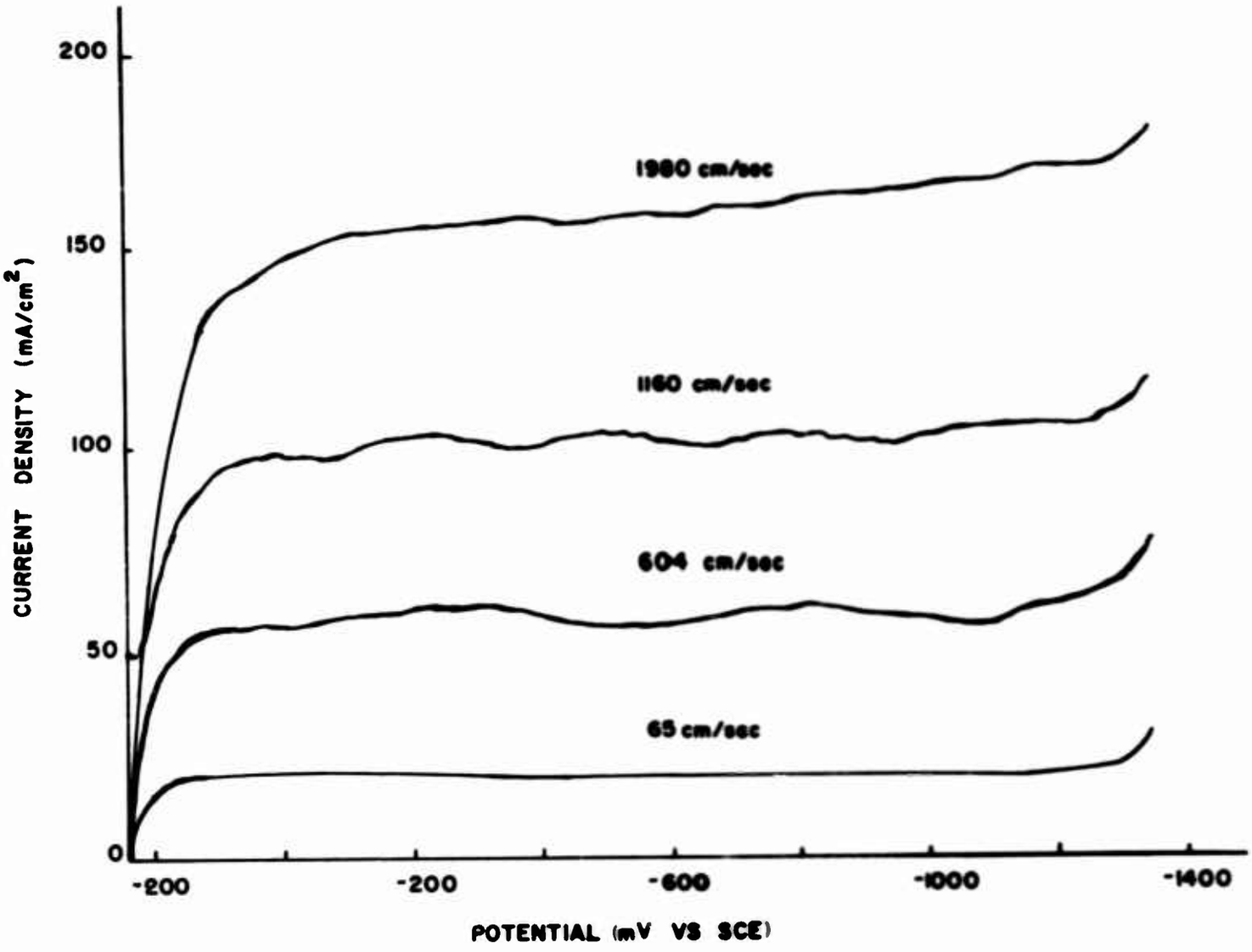


Figure 5. Current Potential Curves for Cathodic Reduction of Ferricyanid at Different Flow Rate. Potential Scan Rate = 100 mV/sec

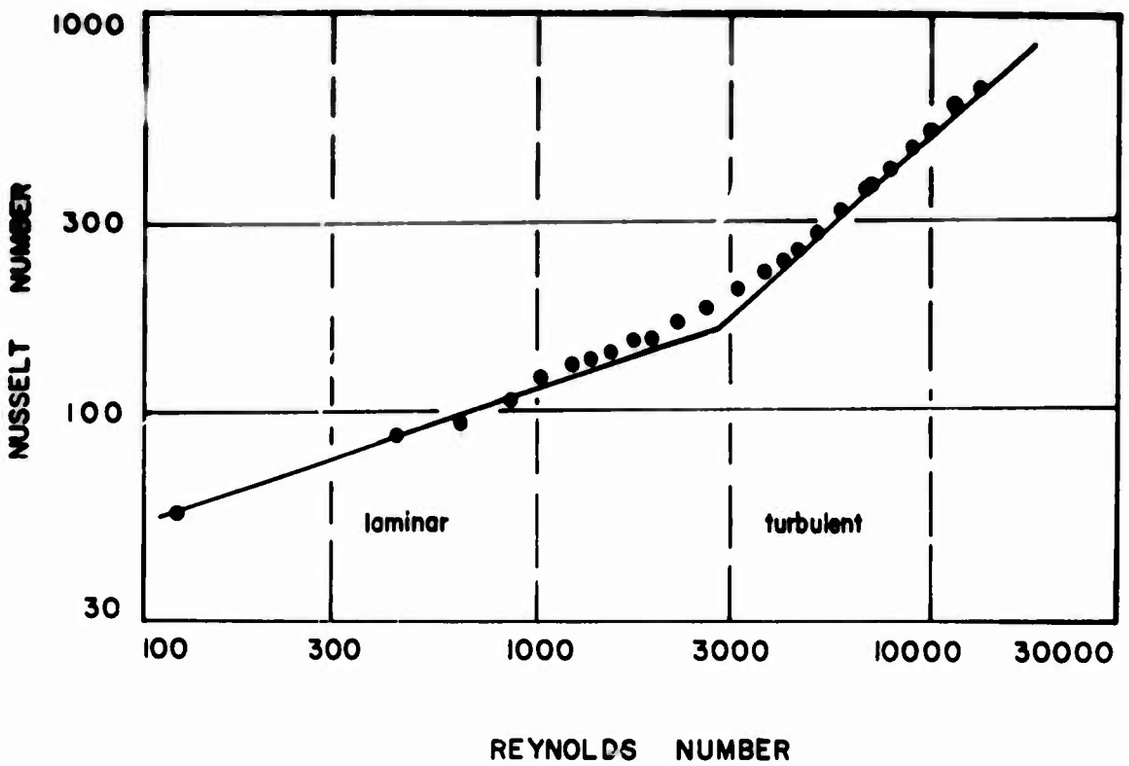


Figure 6. Mass Transfer Characteristics of Flow Channel Cell Derived from Measured Limiting Currents for Ferricyanid Reduction. Solid lines represent mass transfer rates predicted for laminar and turbulent flow by the correlations given in the text.